1 Introduction

Polymer coatings are applied to surfaces (a) to impart desirable properties to the finished product (corrosion resistance, to reduce wear and friction, and to improve appearance), or (b) as part of an intermediate processing step (photolithography, etc.). If the coating is applied as part of an intermediate step, then it is required that this coating be removed prior to subsequent processing operations. Coating removal is also required for recycling/recovery of used or obsolete products (computer chassis, compact discs, etc.). At present, the removal of polymeric coatings is typically done using liquid organic solvents. However, the numerous environmental regulations faced by manufacturers who currently utilize solvents for these applications, and the wide range of concerns pertaining to their environmental release paths, is leading industries to seek less-hazardous, zero-discharge coating removal technologies.

During the last two decades, the concept of supercritical fluids (SCFs) as a solvent has grown out of knowledge developed through supercritical extraction and purification processes. In the U.S., commercial supercritical fluid (SCF) applications include coffee decaffeination, hops extraction, extraction of organic wastes from water, fats from foods, essential oils and spices from plants, and purification processes in the petrochemical industry.[1] While the technology is in widespread commercial use it has dealt primarily with simple molecules that dissolve in fluids such as carbon dioxide (CO_2). Therefore, the current commercial applications can be broadly described as selective extractions of

organic molecules (compounds) from organic matrices. This ability of supercritical CO_2 to solubilize organic compounds has recently extended the scope of applications to include commercial de-greasing and precision cleaning of machined parts contaminated with oil and greases. These cleaning applications are similar to the selective extraction and purification applications in that the objective is to solubilize, and thereby separate, organic compounds from matrices. There are two major differences, however, between these two types of applications. First, in a cleaning application, it is not the bulk of the "matrix" which is subjected to the supercritical fluid, but rather only the (typically inorganic) surface. Second, it is frequently required in cleaning applications that the supercritical fluid solvent not have any deleterious effects on the substrate, in contrast to the selective extraction and purification applications, where the effects on the matrix are generally inconsequential.

The removal of polymer coatings can be considered to be a cleaning application, since it is the selective separation of the polymer from the surface of the substrate which is desired. Also, whether or not the coating removal technique is inert with respect to the substrate will depend on the reason for the coating removal, i.e., whether it is part of an intermediate processing step or part of a recovery/recycling process. Finally, there is one more important aspect to the use of supercritical fluids for the removal of polymer coatings. While the use of organic liquid solvents may achieve the end result of polymer coating removal, it is nearly always the case that a liquid solvent based process does not allow for simple recovery of the polymer, if this is desired. Also, there will nearly always be a waste treatment and/or disposal issue associated with the spent liquid solvent.

This work represents an investigation into the use of supercritical fluids, and carbon dioxide in particular, for the removal of polymer coatings. At this initial stage of coatings removal research, substrate/polymer interactions will not be considered, though those interactions could be significant in some applications. It will be shown in this work that the removal of a polymer coating depends on the dissolution of the supercritical fluid solvent into the polymer, and the resulting swelling of the polymer. Pure, supercritical CO_2 is limited in its ability to dissolve most polymers. Rather, it is the sorption of supercritical CO_2 into a wide variety of polymers and the resulting swelling of the polymer that can be utilized to achieve the desired interactions. In fact, near its critical point, CO_2 is as soluble in many polymers as are typical liquid organic solvents, ranging from (approximately) 10% to more than 30% by mass.[2] Maximizing CO_2 solubility and the subsequent polymer swelling, or disruption of the polymer/polymer interactions, followed by rapid depressurization, causes the polymer coating to fracture and/or debond from the substrate. This research illustrates a method to select the optimum composition of supercritical fluid solvent, which can include not only a pure solvent but also one or more dissolved co-solvents, given a known polymer. Further, the method allows for the prediction of the optimum processing conditions of temperature and pressure in order to achieve maximum polymer impregnation and swelling. This method relies on the use of solubility parameters. Traditionally, the solubility parameter concept has been almost exclusively confined to mixtures of ambient-pressure liquids. It is shown in this work how the solubility parameter concept can be applied to each of the components (pure fluid, cosolvent(s), and polymer) in the liquid, gas, and supercritical fluid states.

The solubility parameter method will be applied to two specific polymer coating removal applications - stripping of hardened photoresist-coated silicon wafers, an example of coating removal as part of an intermediate processing operation, and removal of a photoconductive polymer coating from laser printer drums, which is an example of a recovery/recycling operation.

1.1 Example Application #1: Removal of Photoresist Coatings from Silicon Wafers

The fabrication of integrated circuits (IC) relies heavily on an intermediate processing step called photolithography to define the shape and pattern of individual components.   In the photolithography process, Figure 1-1, a film of photo-reactive polymer, known as a photoresist, is applied to the surface of a semiconductor wafer and cured by exposure to light.   The areas of the photoresist which are exposed to the light source cause the polymer film to undergo either chain scission in the case of a positive-acting photoresist, or chain cross-linking in the case of a negative acting photoresist. Subsequent immersion in a developing solution causes dissolution of that part of the photoresist that has undergone chain scission (for the positive acting polymer) or has not undergone cross-linking (for the negative acting).   This selective dissolution uncovers well-defined regions of the substrate (wafer) surface.   The remainder of the photoresist film is then baked at high temperature to evaporate excess solvent, thereby "hardening" the photoresist so that it can withstand subsequent fabrication steps, such as ion implantation or metal deposition.   Once the subsequent fabrication step has been completed, the hardened photoresist must be removed before the next step in manufacturing can begin. Current techniques for "hardened" photoresist removal utilize

highly acidic or highly alkaline aqueous solutions, or mixtures of regulated organic solvents. To ensure that all traces of organic solvents and inorganic residues are removed from the wafer surface, the manufacturing process incorporates a final rinse step during the photoresist-stripping process. Up to 4 million gallons of water per day are used in the removal and cleaning steps during this process, generating more waste than any other single step in the IC manufacturing process[3]. The production of a complete IC can involve many iterations of the photolithography process as shown in Figure 1-1. The cost associated with the treatment and disposal of this waste, as well as employee health and safety considerations, are driving a search for alternative, environmentally benign, cost-effective solutions.

The Photolithography Process

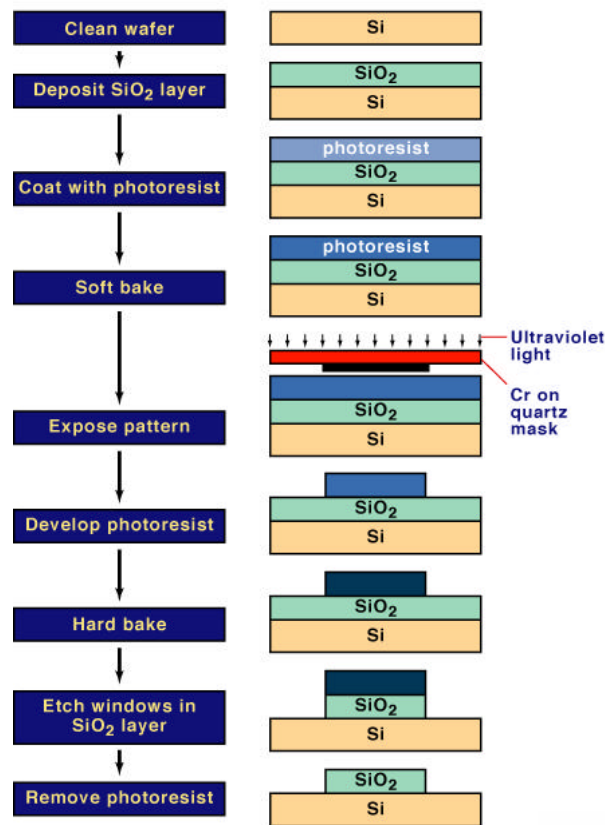|	
Clean wafer	Si
Deposit SiO₂ layer	SiO₂ / Si
Coat with photoresist	photoresist / SiO₂ / Si
Soft bake	photoresist / SiO₂ / Si
Expose pattern	Ultraviolet light / Cr on quartz mask / SiO₂ / Si
Develop photoresist	SiO₂ / Si
Hard bake	SiO₂ / Si
Etch windows in SiO₂ layer	SiO₂ / Si
Remove photoresist	SiO₂ / Si

Figure 1-1. Schematic illustration of the photolithography process, showing the production of a polymer (photoresist) coating onto a silicon wafer substrate, and its subsequent removal.

1.2 Example Application #2: Removal of Photoconductor Coating from Aluminum Drums

The removal of polymer coatings from manufactured components is also important in the application of recovery of improperly coated components or for the recycling of used or obsolete components. At Lexmark International Inc., a global developer, manufacturer, and supplier of laser and inkjet printers and associated supplies, components manufactured for their laser printers are photoconductor drums. Constructed

of anodized aluminum, these photoconductor drums are coated with a charge-generating layer of polyvinyl butyral (PVB) overlaid with a charge transporting film of polycarbonate (PC).

The polymer films, shown in a schematic cross section in Figure 1-2, are applied to a photoconductor drum in a two-step dipping process. The inner PVB coating is affixed by dipping the drum into a 3% solid/97% solvent solution. The solid is 50% PVB/50% pigment, while the solvent is methyl ethyl ketone (MEK). The dip coating is followed by a drying step to evaporate the solvent (100°C for 20 minutes), resulting in a dried PVB coating approximately 1 μm thick. The outer PC layer is applied by dipping the drum into a 20% solid (70% PC/30% transport molecule) and 80% solvent solution (tetrahydrofuran and 1,4-dioxane). Coating is again followed by a drying step (130°C for 1 hour) to evaporate the solvent. The dried PC coating is approximately 25 μm thick.
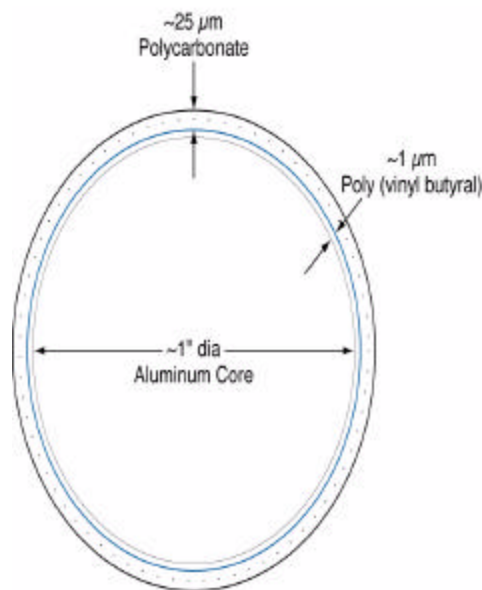

Figure 1-2. *Cross-sectional view of a photoconductor drum with polymer coatings.*

In a laser printing process, also known as electrophotography, the photoconductor drum is analogous to a reusable film. In the printing process, the entire surface of the drum is charged to approximately -800 volts. The laser print head then begins writing characters to the charged drum surface. The charge generation layer, which has a photosensitive dye, undergoes a reaction that produces charge carriers in the local areas addressed by the laser. Due to the presence of the charged drum surface, charge-transport molecules in the transport layer transfer the photo-generated charges to the drum surface. Additionally, the charge transport layer provides protection to the charge generation layer from the abrasion of the paper, cleaning blades, toner, etc. The net result of the charge generation and transport process is the generation of localized regions of lower charge (approximately -150 volts), in the shape of the laser-generated characters on the drum surface. These "discharged" areas attract toner particles, which are also charged, resulting in toner adhering only to specific locations. The toner is then transferred to the paper and fused by a heating element. The drum is then recharged to -800 volts, erasing the latent image, and the entire cycle repeated.

Approximately 5% of the coated drums manufactured by Lexmark are discarded for quality reasons. Of these drums, approximately one-third are rejected due to defects in the aluminum substrate with the remaining two-thirds rejected due to defects in the polymer coatings. Quality control consists of visual inspection of all the drums and electrostatic and print testing on a "lot sample" basis. Removal of the polymer films from rejected drums requires manually stripping the polymer films with hazardous solvents such as tetrahydrofuran (THF) and MEK. Currently, all rejected drums are sent offsite for recycling of the aluminum. Removal of the defective polymer coating would

result in an estimated annual 200,000 reclaimed cores suitable for reuse. In addition, an unknown number of photoconductor drums could be reclaimed from used components returned from buyers following their useful life.

1.3   Research Methodology and Results

Chapter 2 discusses the details of supercritical fluids with an emphasis on supercritical CO_2. It is shown by reference to physical properties why supercritical fluids are useful as processing solvents, and why supercritical fluids are gaining attention for cleaning and polymer coating removal. Also, the different types of macroscopic interactions, such as those leading to the removal of a coating, which can occur between polymers and a supercritical fluid are illustrated by examples where such interactions are, or can be, commercially applied.

Chapter 3 reviews the microscopic forces that operate between the molecules of a pure substance and between unlike molecules in a mixture. The purpose is to give a brief introduction to the nature and variety of forces acting between molecules which must be accounted for in any description of a fluid-polymer processing application.

Chapter 4 introduces the various solubility parameter models which have been used to evaluate the range of molecular interactions discussed in Chapter 3. The development of the solubility parameter methodology and the model chosen for expansion in this dissertation are examined and established.

Chapter 5 make use of the solubility parameter models for expressing the cohesive properties of pure components (solvent, cosolvent(s), and polymer). In addition, because a supercritical fluid application typically operates at pressures far above

atmospheric and at greater than ambient temperatures, the effects of temperature and pressure on the pure component solubility parameter values are considered.

Chapter 6 continues with characterization of solubility parameters of binary pairs of components (solvent/cosolvent, solvent/polymer, and cosolvent/polymer). Other considerations, such as Lewis acid/base interactions between the solvent and polymer or polymer functional group, as well as between the cosolvent and polymer or polymer functional group, are examined.

Chapter 7 is an example of vapor liquid equilibrium modeling with CO_2 and propylene carbonate.

Chapter 8 compares experimental results with the model framework developed.

Chapter 9 is a summary and discussion of the present work, while Chapter 10 contains references.

There are four Appendices included at the end of the dissertation, (A) CO_2 equation of state and respective partial derivatives; (B) CO_2 Ideal solubility discussion, details of the published CO_2 solubility data in 103 solvents, and results of the RED (relative energy difference) calculations; (C) CO_2 HSP Values for a range of pressures and temperature; and (D) Equation of state references.